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# Analysis of Sulfur in the Copper Basin and Muddy River Sites

## **Cover Page Footnote**

Michael Berger and Ling Zou would like to acknowledge Thermo Fisher Scientific for support for this project.

# ANALYSIS OF SULFUR IN THE COPPER BASIN AND MUDDY RIVER SITES USING PORTABLE XRF INSTRUMENTATION

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## ABSTRACT

The feasibility of using a portable analytical instrument, the Niton XRF XLt 500He, was tested as a technique for sulfur analysis of wet sediment samples in the field. The effect of sample preparation on the precision and accuracy of sulfur determination was specifically evaluated. The Niton XRF XLt 500He uses X-ray fluorescence (XRF) to detect different elements. This unit employs a helium purge to allow the analysis of elements lighter than potassium. Samples with sulfur varying from 0.3 to 2.0% were successfully measured with the instrument. The precision of the unit is excellent and the limit of detection can be extremely low with careful attention to sample preparation. The instrumental limit of detection for sulfur was estimated as 70 ppm.

Keywords: X-ray fluorescence, sulfur, sediment, moisture content

## 1. PURPOSE OF THE STUDY

Experiments were conducted to determine to what accuracy and how precisely sulfur could be determined in sediment samples using a portable Niton X-ray fluorescence Model XLt 500He. This unit has been modified by NITON Analyzers (NITON) to allow a flow of helium to displace the ambient air present in the instrument, especially in the areas of the sample and detector. Portable field analyzers using X-ray fluorescence (XRF) are normally limited to the quantitative analysis of elements heavier than potassium, because air and moisture effectively scatter the weaker fluorescence from the lighter elements. Since helium does not appreciably scatter or absorb sulfur X-ray fluorescence, it was hoped that the helium purge method would allow better limits of detection and quantitation of sulfur in a portable analyzer.

## 2. INTRODUCTION

The presence of sulfur in soil can present potential risks of harm to human health and the environment. The Copper Basin, located near the junction of Tennessee, Georgia, and North Carolina, and the Muddy River in Boston, Massachusetts both present significant levels of sulfur (S) in soils and sediments. The Copper Basin was once an active mining site and the elevated sulfur presence there is a result of pollution from the mining activities. These elevated levels of sulfur can create high levels of acidity in water runoff, causing detrimental effects on the natural habitat and environment. The first step in the remediation of this site is a determination of the

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spatial extent of soils with greater than 2% sulfur, soils which are thought to have the greatest potential for acid mine drainage. XRF was used for the analysis of sulfur in the Copper Basin tailings. The Muddy River is the backbone of the Emerald Necklace, an historic landscape surrounding Boston, Massachusetts. Over the years, the Muddy River has accumulated large quantities of sediment, consisting of decaying vegetation, sand from stormwater drains, and riverbank erosion. These sediments are contaminated with high levels of metals and petroleum hydrocarbons. (CDM, 2001) Varying amounts of sulfur have been detected in the sediments. With limited availability of oxidants in the sediments sulfur can be released as hydrogen sulfide, which is toxic to fish and when volatilized unpleasant to humans at extremely low concentrations in air. Dredging of the river is planned for the near future and may release harmful levels of hydrogen sulfide into the air and water. The selection of a remediation strategy for the river that minimizes sulfur volatile emissions during sediment dredging operations could be guided by a sulfur analysis of Muddy River sediments. Portable XRF represents a convenient analytical option. Our study evaluates the suitability of the Niton XRF XLt 500He as a portable handheld instrument for sulfur quantitation.

Earlier studies (Richter, 2005) of tailings from the Copper Basin analyzed sulfur content with a portable XRF unit without a helium purge and showed promising results. Moist silty samples containing from 1 to 6% sulfur were analyzed with the aid of a special filter optimized for light elements. Calibration of the device was shown to be possible by taking into account the iron content of the sample, and a complex calibration was found to work with a number of different samples. However the signal/noise was low, and the device offered the best performance for samples with high levels of sulfur. Improvements in the technology and the inclusion of a helium purge in the instrument by the manufacturer increased the signal/noise by a significant amount and promised semi quantitative analysis of samples with lower amounts of sulfur, such as sediments.

There are several well established methods for the analysis of total sulfur in soil, including combustion in an oxygen bomb (Parr Instruments, Bailey and Gehring, 1961) followed by analysis of the sulfate produced or alkaline oxidation followed by X-ray fluorescence (Tabatabai and Bremmer, 1970, Perrott et al, 1991). However XRF for sulfur analysis normally requires high vacuum pumps to eliminate the scattering effects of the air. These devices are not suited for portable use due to the size of the instruments and the supporting operational requirements, such as power and vacuum pumps.

The US EPA considers XRF a valid soil screening method (USEPA Method 6200, 1998) for dried soils and sediment. However, the Environmental Technology Verification Program (NEWMOA, 1999) noted “a high moisture content can interfere with the analysis. In situ analysis cannot occur if there is ponded water. For ex situ semi-quantitative analysis, if the moisture content is greater than approximately 20%, then the sample should be air dried.” The use of XRF as a screening tool for wet marine sediments was not fully verified until an Environmental Security Technology Certification Program (ESTCP, 2000) project demonstrated good results from XRF analyses of unprepared wet sediments. Our study examines the effects of moisture content up to 50% commonly found in sediments.

Non-portable XRF instrumentation continues to be used for the analysis of sulfur in sediments and minerals (Seider, 2007). Sommer used a non-portable XRF instrument to analyze sulfur in dried sediment samples collected from suburban wetlands surrounding Lake Goollal in the Swan Coastal Plain of Australia. (Sommer, 2006). While there have been several studies

of sediments with portable XRF instrumentation, many did not analyze for sulfur (Dooley and Stallard, 1994, Ferry and McArthur, 2002), but focused instead on heavy metal content. A specialized and high resolution application of XRF technology used to analyze sediment cores, XRF-CS, has recently been developed to analyze both wet and dried sediment cores for sulfur and other elements (Etoubeau et al, 2009). These XRF devices, while mobile, are often installed on sea-faring research vessels, and are significantly more complex than (handheld) portable XRF devices.

### 3. MATERIALS AND METHODS

In this study, we compared the sulfur analyses obtained by the Niton XRF XLt 500He with the analyses of similar samples using the oxygen bomb method to oxidize the sulfur, followed by sulfate analysis. Samples with certified sulfur concentrations were used for calibration. Sediment samples were run with and without the helium purge in the Niton XRF Model 500He in order to determine the degree of improvement in the signal detection attributable to helium's elimination of scattering by atmospheric gases.

The theory of X-ray fluorescence has been described previously (Jenkins, 1999). The X-ray sulfur fluorescence occurs from 2.2 to 2.4 keV and is relatively free from interference attributable to fluorescence from other elements or to excitation lines from the source.



*Figure 1.* The Niton XLt 500 He system with sample stand, analyzer, and Helium purge.

The Thermo Fisher Scientific Niton XLt 500He system uses the helium purge technique in a portable/handheld format. The analyzer has a sealed measurement head that is purged at 150 mL/min with pure helium to displace air from the X-ray analysis path, allowing the light element fluorescence X-rays to reach the detector. The analyzer uses a 40 Kev miniaturized X-ray tube and can determine, using K shell radiation, elements Mg to Ba and L shell radiation for elements Cs to U.

The XRF signal can be significantly influenced by the preparative technique (Pasmore et al, 2005, Shefsky, 1997). For the most precise work, drying the sample to eliminate water, followed by grinding and sieving to 120 mesh is recommended (NITON, 2007). The advantages of this procedure are: representativeness of the sample is excellent since homogeneity is achieved and intimate contact and flatness of the sample produces the highest and most reproducible fluorescence. Our study evaluated the importance of sample preparation and the effect of sample water content on the sulfur analysis, since it is not always convenient to dry, grind, and sieve the sample in the field. We studied whether the presence of water presented additional unique analytical problems in the analysis of the lighter elements with the Niton XRF Model 500He compared to the analysis of the heavier elements.

Elements heavier than potassium are excited by X-rays in the 5 to 40 keV range. The X-ray excitation of heavier elements penetrates a couple of millimeters into the sample, and the fluorescence readily passes back through a thickness of the sample before being detected. However X-rays used to excite the lighter elements, like sulfur, are only 5 keV and thus will only pass only a few microns into the sample. (Jenkins, 1999, Thermo Electron Corporation, 2005). The resulting X-ray fluorescence will also emerge from only the top few microns of the sample. In recognition of the “weak” penetration of X-rays involved in the analysis of lighter elements, sediment samples were prepared with a thinner sample covering – 4 micron thick clear polypropylene cover. This thin cover protects the source and detector from the sediment sample. The cover also is used in the preparation of the sample “cup” which provides a clear “window” covering for the soil. In comparison a clear 6-micron Mylar cover is recommended (NITON, 2007) for analysis of the heavier elements.

Several experiments were conducted to determine what factors influence the accuracy of the sulfur analysis using the portable XRF XLt 500He. Certified soil and sediment standards containing a range of total sulfur content (0.3% to 2%) typically found in sediments were analyzed. Sediment samples from two distinctly different sites on the Muddy River were collected for analysis in this study. Site #3 is characterized by significant petroleum hydrocarbon contamination within the last decade from an historical oil release of Number 2 fuel oil, while Site #6 is characterized by sediment from bank erosion, organic matter, and catch-basin storm-water. Surficial sediment samples from both sites were collected within the top six inches of sediment. Samples from both sites were prepared by comparable methods and analyzed similarly. (See RESULTS Section.) Table 1 summarizes the sediment characteristics of the two sites.

*Table 1.* Characteristics of Muddy River Sample Sites #3 and #6

<b>Site #3</b>	<b>Site #6</b>
Major components – organic matter, petroleum hydrocarbons, silt	Major components – sand and organic matter
Color – dark gray	Color – light beige
Analysis – 1.8% sulfur	Analysis – 0.4% sulfur

## 4. SUMMARY OF EXPERIMENTS

### 4.1 The Significance of Water Content and Sample Preparation

Experiments were conducted to determine the effects of water content in soil and sample preparative techniques on the determination sulfur in sediment samples. The effect of significant water content in sediment samples and the effect of particle size homogeneity were studied. Four sample preparative methods were studied to determine the effect on the resulting analytical results. Table 2 summarizes the different Sediment Methods described above.

*Table 2.* Summary of Sediment Sample Preparation

	<b>Dried?</b>	<b>Ground?</b>	<b>Water</b>
Method 1	Yes	Yes	Added to dry sample
Method 2	Yes	No	Added to dry sample
Method 3	No	No	Dried to differing degrees
Method 4	No	No	Excess water blotted

### 4.2 The Effect of Water Content on Other Elements

Samples prepared by the methods shown in Table 2 were also analyzed for other “light” elements and for iron, a typical “heavier” element found in sediments to determine if the conclusions based on sulfur data could be generalized to other elements.

### 4.3 The Benefit of Helium for Analysis of Sulfur

Samples were analyzed for sulfur with and without helium flow in order to determine the magnitude of the expected benefits (i.e., increases signal and decreased noise) of the helium “purge”.

### 4.4 Accuracy of Sulfur Analysis with Portable XRF

In order to determine the accuracy of the sulfur analysis, identical samples were analyzed using an alternate method for the determination of total sulfur to compare to the results obtained with XRF. The “oxygen bomb” method (as modified below) is relatively inexpensive and has been used for many years for the successful determination of sulfur in a variety of materials. One of the goals of this paper is the comparison of the accuracy and the precision of sulfur concentrations in sediments determined by portable XRF and the oxygen bomb method.

## 5. RESULTS

### 5.1 Calibration of the Niton XRF XLt 500He

Standard sediments samples, with known and certified composition were used for calibration of the Niton XRF XLt 500He. Data for all experiments consisted of counts (of X-ray fluorescence) detected per second. Additional experiments were conducted to quantify the signal to noise ratio (S/N) as a function of total signal acquisition time. For the Studies (A) – (C), total acquisition times were kept constant nominally at 240 seconds for Sulfur and other “light” elements, and 60 seconds for the “heavier” elements. Filtration and X-ray tube operating conditions are set up in the instrument to individually optimize excitation of the light and heavy elements in order to maximize the signal to noise ratio. Different sediment and soil “standards” containing certified levels of sulfur were used to calibrate the Niton XRF XLt 500He. Table 3 shows the fluorescence level in counts per second (cps) for different concentrations of sulfur. These data were used to create calibration curves. Different calibration curves were used to best match the actual sulfur concentration present in the sediments tested. The two ranges of sulfur found in the sediments best matched the calibration curves in the range of 0 to 0.3% (low) or 0 to 3.0% (high) as shown in Figures 2 and 3.

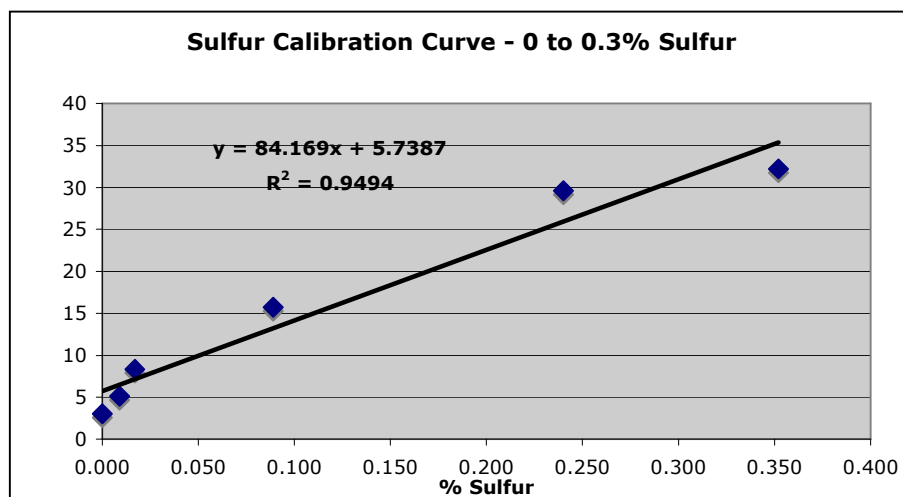


Figure 2. XRF calibration at low sulfur concentrations

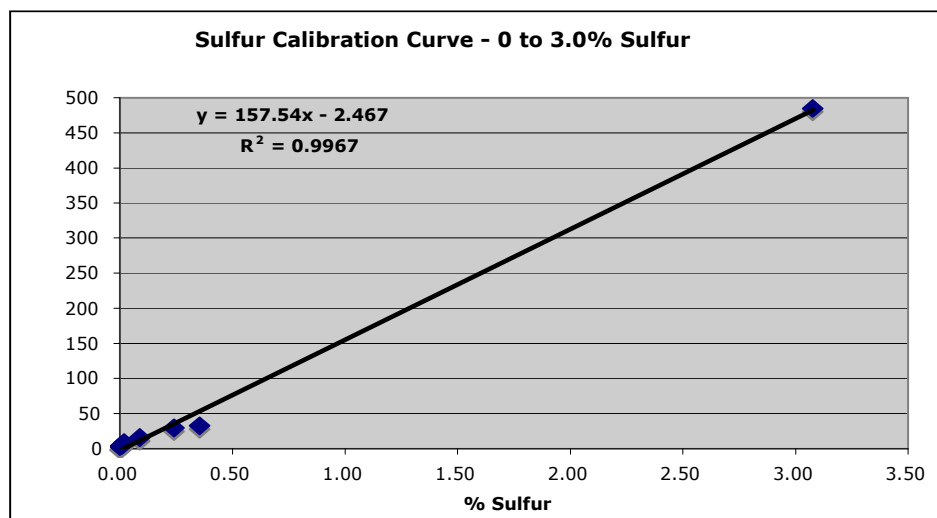
The limit of detection is a measure of the sensitivity of the analytic method and its determination has been described (Harris, 2007). The limit of detection is defined as the three times the standard deviation of a blank sample divided by the slope of a calibration curve for that sample. For this determination a silica standard certified as 99.999% pure was used as the blank. In the case of XRF analysis of sulfur, the limit of detection was 0.0071% or 71 ppm. It should be noted that this is an “instrument detection limit” which is a measure only of the magnitude of stochastic variability in the XRF device. Of course, the “total measurement error” (Shefsky,



1997) determines the method detection limit (MDL). The MDL is determined by the total measurement variance, which is the sum of the variances due to analytical instrumentation, sample representativeness, sample preparation, and sample handling. The MDL is used for regulatory purposes since it takes into account all variability encountered in measuring an analyte. While experiments were not conducted to determine the MDL, method variables such as moisture content and sample preparation were found to significantly affect the results.

*Table 3. Certified Standards used for Calibration of XRF*

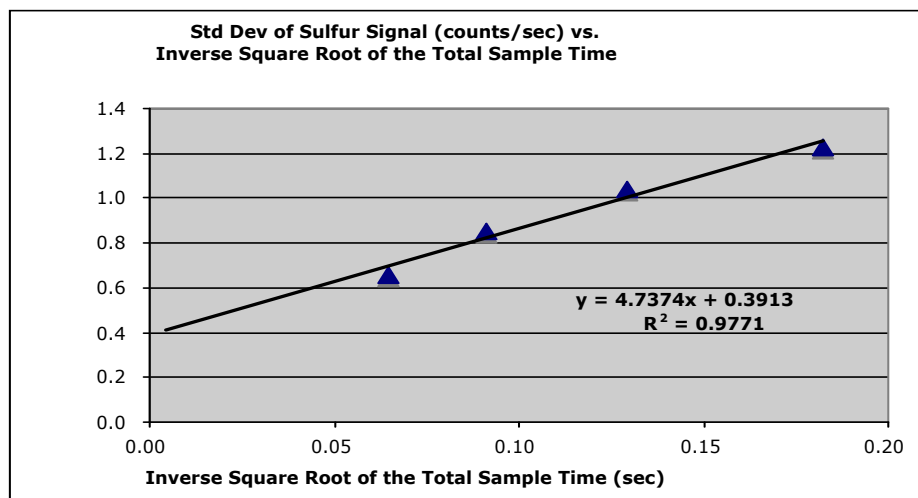
<b>Sample</b>	<b>S cert. %</b>	<b>S cps</b>
99.999% Silica	0.00	2.99
NCS DC73308	0.01	5.09
NCS DC73309	0.02	8.33
NIST2709	0.09	15.71
NIST2710	0.24	29.59
NIST 1646a	0.35	32.23
NIST 2684b	3.08	484.78



*Figure 3. XRF calibration at high sulfur concentrations*

## 5.2 The Effect of Sampling Time on Signal/Noise:

As predicted by statistical considerations, the standard deviation of the sulfur signal decreases as the sampling time is increased. Figure 4 shows the expected relationship between the standard deviation and the inverse square root of the sampling time. (It is assumed that the total sample excitation is directly proportional to the sampling time for constant excitation power.)



*Figure 4.* Standard deviation of sulfur fluorescence as a function of the inverse square root of the total sample time

The non-zero intercept indicates that there is a significant contribution to the standard deviation of the sulfur signal that does not arise from stochastic events involved in excitation of or fluorescence from sulfur in the sample. While data collection for longer times does improve the signal to noise ratio, a significant component of noise remains even at longer measurement times. The portability of the XRF XLt 500He permits data collection in the field. In field situations, measurements at shorter times allow a large area to be screened in a relatively short period of time. In this case, it may be more important to have data from many samples with a larger standard deviation, than data from fewer samples that have a smaller standard deviation. In general, we found that collecting fluorescence data with the XRF XLt 500He for a period of four minutes improves the S/N by a factor of two over data measured for only 30 seconds. Only additional slight improvement in signal to noise (S/N) can be realized by data measurements longer than 4 or five minutes.

### 5.3 The Significance of Water Content and Sample Preparation

#### 5.3.1 Preparative Method 1

Sediment samples were placed in an oven overnight at 60°C to dry completely, then ground with a mortar and pestle and passed through a 120 mesh screen. Samples with different water content were prepared by adding varying amounts of organic-free water to the dried sample with thorough mixing. Sediment samples were prepared with water content varying from 0 to 50% w/w. Figure 5 shows XRF data of sediments with different water content in a portion of the Muddy River with approximately 0.30% sulfur (Site #6). The magnitude of the sulfur X-ray fluorescence decrease with increasing water content can be modeled as a simple dilution of the sediment with the added water; the sulfur fluorescence is practically halved (44% decrease) as the sample is diluted to about 50% with added water.

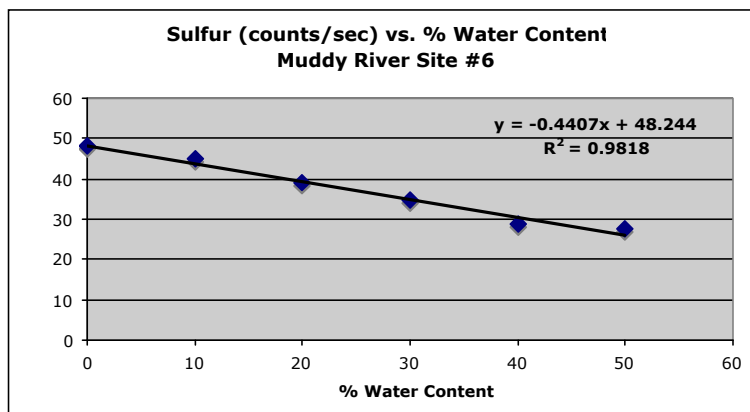


Figure 5. Sulfur (cps) versus water content for Method 1

### 5.3.2 Preparative Method 2

Sediment samples were placed in oven at 60°C overnight to dry completely, then simply forced through a coarse screen approximately 60 mesh in order to remove stones, sticks, and leaf fragments. The effect of water on the analysis was studied by adding organic-free water to the dried sample. Comparison of the results from Method 1 and Method 2 show how important particle size and homogeneity is for sulfur analysis of sediment samples. While both methods show a dilution effect as water is added to the dried sediment, the effect is much larger for the coarsely sieved sediment; the sulfur fluorescence decreased 76% with the addition of 50% water by weight in Method 2 - considerably more than with Method 1. Note in Figure 6 that  $R^2$  for Method 2 is significantly poorer than for Method 1, probably due the greater heterogeneity and roughness of the samples created with Method 2. A flat and homogeneous sample surface is necessary for quantitative XRF analysis, especially for the lighter elements, since the weaker fluorescence of the lighter elements is greatly attenuated on its way to the detector. Surface roughness is also a factor when considering light element analysis. For light elements only the top layer of the sample contributes to the analysis, and therefore that top layer must be representative of the bulk sample. (Thermo Electron Corporation, 2005).

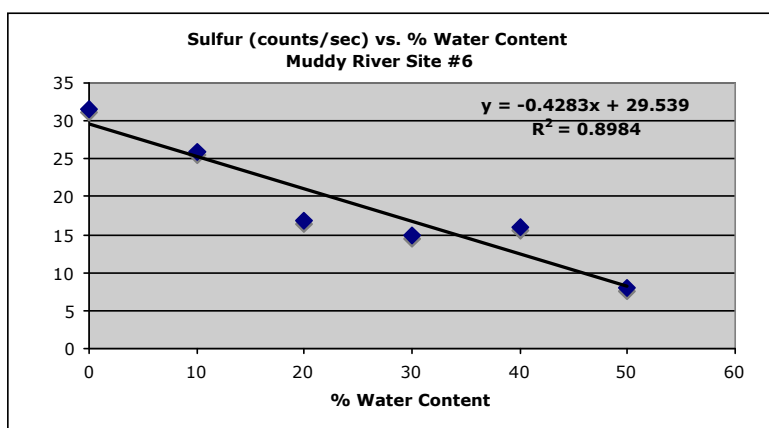


Figure 6. Sulfur (cps) versus water content for Method 2

The effect of sample preparation in this study is clearly shown by the different preparative methods. The effect of larger particle size (Method 2 versus Method 1) is to reduce the sulfur fluorescence by almost 40%, and increased moisture causes a further significant reduction. (Figure 6). The present study also shows (below) that the fluorescence of different elements is affected to a different degree by the presence of water. In order to minimize the total measurement error and to reduce the method detection limit, it is important to prepare the sample in the lab as recommended by the XRF instrument manufacturer and to generate calibration curves that account for the effect of water content and grain size for each element of interest.

### 5.3.3 Preparative Method 3

Wet sediment samples were passed through a coarse screen (approximately 60 mesh) to remove bulky particles, then put in an oven at 60°C for different lengths of time to obtain samples of different water content after heating. In this case, no water was added to the sediment as was the case for Methods 1 and 2. Figure 7 shows that the linear regression for Method 3 is not as good as that obtained with Method 1 or Method 2. The greater heterogeneity of Method 3

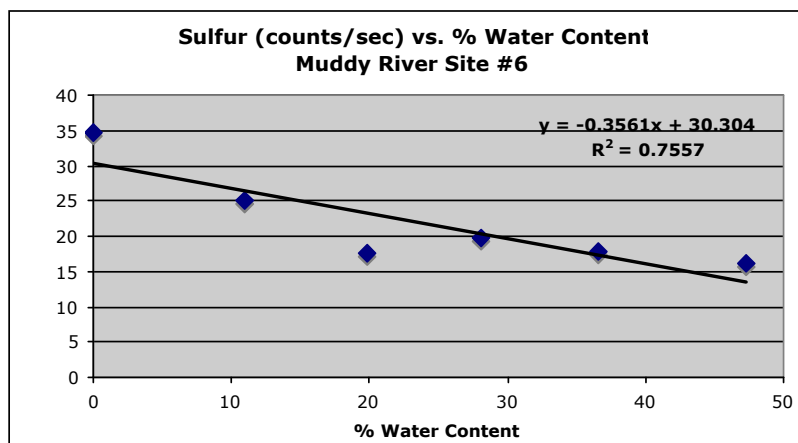


Figure 7. Sulfur (cps) versus water content for Method 3

may be the cause of greater scatter in the regression. The estimate of the quantity of sulfur extrapolated to zero % water content is similar to that of Method 2 – only 60% of the “dry” quantitation extrapolation using Method 1.

Methods 1 – 3 were also used to evaluate the sediment obtained from a different section of the Muddy River, Site #3. While analysis (below) showed that sediment samples from Site #3 had considerably more sulfur than samples from Site #6, the conclusions about the effect of water content on sulfur analysis were the same for both Sites. Figure 8 shows the effect of sample preparation for the different methods on the precision and accuracy for Muddy River Site #3.

### 5.3.4 Preparative Method 4

This sample preparation method is a very simple procedure that could potentially be used in the field. Wet sediment samples were passed through a coarse screen (approximately 60 mesh) to remove bulky particles, then simply blotted for about 30 seconds with a paper towel to remove water as much water as possible. Each sample was then assembled in a measurement cup with the sediment still in contact with the paper towel. Five replicate samples were prepared and sulfur counts/sec (cps) recorded normally with the Niton XLt 500He (Filter 2 for 240 seconds). The mean sulfur cps was 109.1 with a standard deviation of 7.8 cps. The sulfur fluorescence was only 53% of the “dry” sample determined by Method 1. The results of this test indicate that Method 4 can give reproducible sulfur content based on wet weight, but will naturally report a sulfur content lower than that of a thoroughly dried sample.

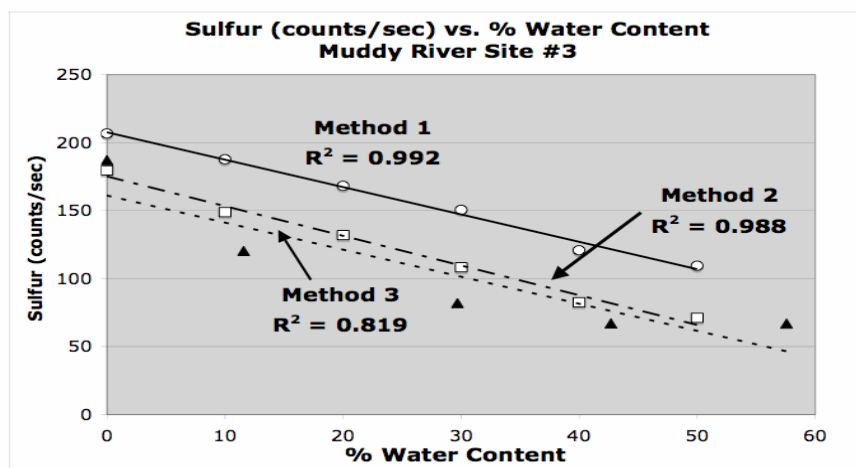


Figure 8. Effect of sample preparation on precision and accuracy – Site #3

The use of paper towels to remove moisture from samples has been studied recently (Markey et al, 2008) with soil samples for the analysis of lead. A good correlation was reported with dried and sieved samples.

#### 5.4 The Effect of Water Content on Other Elements

The effect of water content in the sediment on the detected fluorescence was studied for a number of different elements. Figure 9 shows the relative detected fluorescence of a “wet” sample compared to a thoroughly dried sample using Method 1. The “dilution” effect of water on the dry (maximum) signal varied with the element. While the X-ray fluorescence from iron only decreased 23% when the sample contained 50% water, aluminum, silicon, and phosphorus and sulfur X-ray fluorescence decreased approximately 50% with a dilution of 50% by water. The background fluorescence for all elements was assumed to be zero, but in reality, there is a background fluorescence that must be subtracted for each element for the most accurate work. The different background levels may account for the apparent differences in the effect of water. For the most accurate study, it is important to characterize the background and the “dilution” effect of water content for the samples of each element.

Our observations on the effect of moisture content qualitatively agree with those of Dooley and Stallard (1994) who used XRF instrumentation to analyze metals in San Diego Bay sediments with 30% to 60% water content. They concluded that the variations in concentrations between wet and dry samples did not simply correlate with water content. They found that while the ratio of fluorescence from wet samples was about 50% that of dried samples for lighter elements, approximately equal fluorescence intensities were obtained from wet and dry samples for the heavier elements. They did not analyze for sulfur. Figure 9 shows that for our study the attenuation of the fluorescence by water is indeed greater for the lighter elements than for the heavier elements.

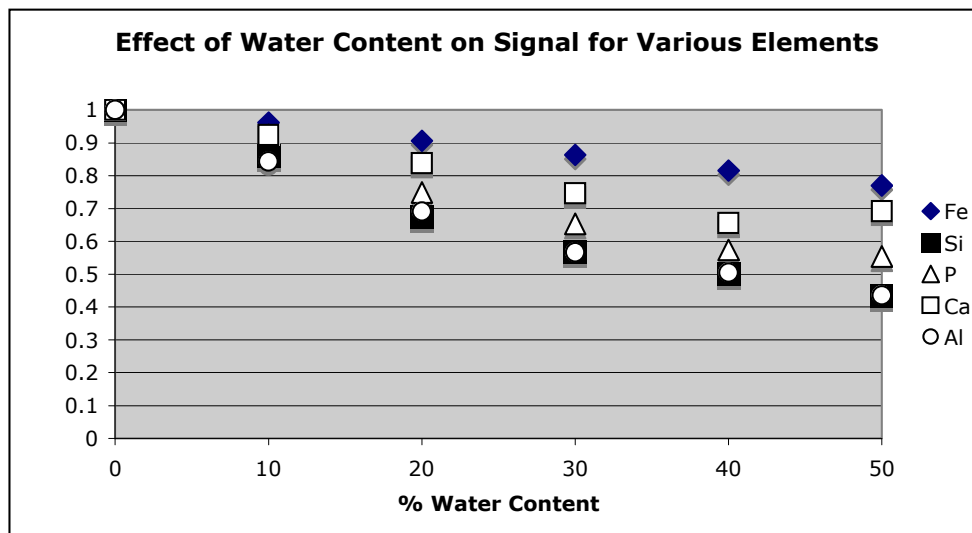


Figure 9. Effect of water content on X-ray fluorescence for elements other than sulfur

### 5.5 The Benefit of Helium for Analysis of Sulfur

The effect of the helium on S/N was determined by calculating the relative standard deviation (RSD in parts per thousand, ppt) for a sediment standard with a low concentration of sulfur, NIST 1646a with 0.35% Sulfur. The RSD for the sample with helium was 19.9 ppt, compared to an RSD of 28.3 ppt when the helium was not used, a 30% improvement in RSD that is attributable to the helium purge. While the benefit of helium was noted for sulfur for several different samples, the improvement was quantified for several elements in a dried and sieved (120 mesh) sample of Certified Standard 1646a. Table 4 shows that the benefit of helium is greater for the lighter elements, and there is only a minimal improvement in fluorescent intensity or relative standard deviation (RSD) for the heavier elements.

The less energetic fluorescence from the lighter elements is attenuated by the water vapor and oxygen in the air. The helium purge displaces the water vapor and oxygen in the region of the detector, thereby increasing the signal. On the other hand the more energetic fluorescence from the heavier elements is only slightly attenuated by water vapor and oxygen in the air, and thus helium has a small effect.

Table 4. Effect of Helium Purge

Element	Helium CPS Increase (%)	Helium RSD Reduction (%)	K $\alpha$ (KeV)
P	252	47	2.02
S	104	30	2.31
K	27	11	3.31
As	8	3	10.54
Fe	3	1	6.40

## 5.6 Accuracy of Sulfur Analysis

There are several methods to analyze sulfur and the sulfate resulting from the oxidation of sulfur (Eaton and Franson, 2005). The sulfur analytical methods used in this investigation are described in this section. In order to determine the accuracy of the portable XRF device, sulfur determinations using the Niton XLt 500He were compared to results using the “oxygen bomb” method. While the XRF method reports the concentration of sulfur directly to the user in a single step, the oxygen bomb method first requires combustion of the sample and subsequent analysis of the combustion residue as described below in order to determine the sulfur concentration in the original sediment sample.

An oxygen bomb (Model 1108 Oxygen Combustion Bomb, Parr Instrument Company, 211 Fifty-Third Street, Moline, Illinois 61265 USA) was used to oxidize the sediment samples and the combustion methodology described (Parr Instrument Company) was followed closely, except as noted below. In this method, one gram of the sediment was exactly weighed and finely ground to make a pellet with a compression press (Model 2811 Parr Pellet Press). The pellet was reweighed before placing it in contact with a wire fuse and then placed into the stainless steel bomb. One to five milliliters of organic-free water was added to the bomb before final assembly in order to provide a “sink” for the conversion of oxidized sulfur as SO<sub>2</sub> into sulfate as sulfuric acid. After assembly, pure oxygen was admitted up to a pressure of 30 atmospheres in order to provide sufficient oxygen for complete combustion of the pellet. The fuse was ignited with the application of an electric current that in turn initiates the combustion of the pellet. The sulfur is then oxidized to sulfate, which is recovered quantitatively by washing the residue from the spent bomb. Depending on the concentration of sulfur in the sample, 250 mL to 500 mL of organic-free water was used for rinsing the stainless steel bomb after combustion. The washings containing the sulfate were analyzed using both the turbidity method (Hach, 2004) to quantitate sulfur, or using ICP - AES. The ICP - AES analysis was performed by VHG labs, Inc., 276 Abby Road, Manchester, New Hampshire.

Initial tests with calibration sediment sample 1646a in pelletized form showed evidence of incomplete combustion. Since the calibration sediment standard had a low percentage of organic content it was thought that the bomb did not completely ignite due to insufficient heat. Upon the recommendation of Parr, Inc. (private communication with Parr Customer Service, July 2, 2007) a couple of drops of mineral oil were added to the pellet before ignition. However, based on observations of the pellet after combustion, and based on the recorded temperature rise in the calorimeter, mineral oil was rejected as an ignition aid. Instead, naphthalene was selected as an ignition aid for two reasons: naphthalene has a high heat of combustion, 9.62 kcal/gram (Atkins and Paula, 2006) and it can be obtained with high purity, thereby contributing no sulfur to the

residue and washings. Blanks consisting of approximately 0.9 gram of naphthalene with no sediment were combusted in the oxygen bomb and analyzed for sulfur; the blanks yielded no detectable sulfate as analyzed by the turbidity method. However, a small and variable amount of sulfur was detected with the combustion of the naphthalene blank in the washings when analyzed by ICP-AES; this blank was used to correct the sulfur values for the baseline tests summarized in Table 5, below. It was found that consistent combustion based on a consistent increase in the calorimeter temperature and by visual observations of the residue was achieved with one gram sample pellets prepared from a mixture of sediment and naphthalene in a 2:1 w/w ratio. Based on these results, naphthalene was selected as a combustion aide and added to all standard and sediment samples for oxygen bomb combustion.

The sulfur concentration in the original sediment sample was calculated based on the sulfate concentration of the washings from the oxygen bomb combustion. The procedure for sulfate determination from bomb washings described by Parr Instrument Company was modified. Parr's procedure (Parr Instrument, 2007) specifies boiling the residue and washings from the spent oxygen bomb in a platinum crucible with hydrochloric acid before analysis of the sulfate. While this step was not performed, satisfactory results were obtained based on the results from calibration standards. Upon combustion in oxygen, it is assumed that one mole of sulfur produces one mole of sulfate, and one mg of sulfur produces three mg of sulfate. Two methods were used to determine the sulfate concentration in the bomb washings.

The turbidity method for sulfate (Eaton and Franson, 2005) is based on the decrease in light transmission due to the formation of a fine dispersion of precipitated barium sulfate when a test sample containing sulfate is added to barium chloride. The turbidity determination is usually regarded as semi-quantitative, since the amount of the decrease in light transmission due to light scattering from the barium sulfate precipitate is sensitive to several factors: other constituents in the unknown solution, the specific conditions of precipitation – such as agitation and temperature, and the elapsed time between the beginning of the analysis and the final light transmission reading. Turbidity measurements were performed using the Hach DR/890 Colorimeter following the procedures described for the Sulfa Ver 4 Method (Hach, 2004). Best results were achieved using the “user calibration mode” calibrating between 10 and 50 mg/L sulfate. Samples with concentrations greater than 50 mg/L sulfate were diluted so that the resulting concentrations fell within the calibrated range of concentrations. Hach (2004) reports the precision of the sulfate turbidity test as  $\pm 3$  mg/L. The user calibration curve prepared with 8 standard sulfate solutions gave a  $R^2$  goodness of fit value of 0.946. It was essential to prepare a new calibration curve for each lot of barium chloride ampules used in the Hach turbidity analytical method.

Samples of bomb washings were also analyzed by ICP - AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy). Table 5 compares the results of sulfur determinations in the washings for five replicate bomb combustion experiments comparing the results from the turbidity and the ICP - AES methods for sulfate (and thus sulfur). The original sample was a certified sediment standard “1646a” with 0.352%  $\pm$  0.004% sulfur. Based on this test of five samples, the standard deviation of the turbidity method is 0.0074%, while the standard deviation of the ICP - AES is smaller, at 0.0046%. The turbidity method is biased 18% low, while the ICP - AES method is biased 15% low. Both methods appear to be biased low. Possibilities for this bias may be due to the modification and simplification of the oxygen bomb procedure used for this work. The residue digestion described (Parr Instrument, 2007) with concentrated



hydrochloric acid in a platinum crucible was not conducted for our experiments. The turbidity method may have an additional negative bias due to settling or agglomeration of the barium sulfate produced in the method.

*Table 5.* Comparison of % S for Turbidity Method and ICP – AES With Modified Oxygen Bomb Method

	<b><u>Turbidity</u></b>	<b><u>ICP</u></b>
	0.2923	0.306
	0.2959	0.299
	0.2966	0.304
	0.2818	0.297
	0.2818	0.295
	0.2897	0.300
<b>Std Deviation</b>	<b>0.0074</b>	<b>0.0047</b>
<b>Bias</b>	<b>-18%</b>	<b>-15%</b>

Table 6 compares the sulfur analyses carried out by different methods. The known % for sulfur is given (if known). Two XRF results are given in the Table: “low S” based on a calibration with standards from 0 to 0.35% sulfur and “high S” based on calibration with standards from 0 to 3.076% sulfur. The analysis based on the oxygen bomb method use the ICP analysis of the bomb combustion products to determine the sulfur %. Sample 1646a is a standard sample with a certified sulfur percentage of 0.352%. The Sediment samples (Sed#3 and Sed#6) have unknown true sulfur values, and the bomb and XRF analyses were conducted on dried and ground samples. Sediment #3 was analyzed to have a sulfur concentration of 1.85%, while the XRF analyses varied from 2.56% to 1.41% based on which calibration graph was used. The “high S” calibration was more appropriate, since Sediment #3 had a concentration of sulfur of 1.85%. On the other hand, the “low S” calibration graph was used for Sediment #6 since it had a sulfur concentration of 0.415% as determined with the oxygen bomb method.

*Table 6:* Comparison of Sulfur Analyses (w/w%)

	<b>True Value</b>	<b>XRF</b>	<b>XRF</b>	<b>Bomb*</b>
<b>Sample</b>		<b><i>low S</i></b>	<b><i>high S</i></b>	
1646a	0.352	0.315	0.22	0.327
Sed #3	Unknown	2.56	1.41	1.85
Sed #6	unknown	0.504	0.322	0.415

\*Sulfur based on ICP analysis of bomb combustion product

## 6. DISCUSSION AND CONCLUSIONS

The effect of water in sediment samples on the analysis of sulfur with the Niton XRF XLt 500He appears to be linear; that is, the sulfur XRF signal decreases linearly with the water content, apparently due to simple dilution of the sample with water. Highest precision and the best accuracy are achieved by the sample preparative technique recommended by Niton (Niton,

2007) the sample should be dried and ground to pass through a 120 mesh sieve. An increase in water content leads to a decrease in the detected sulfur fluorescence signal (a dilution effect resulting in decreased accuracy) and an increase in the variance of the fluorescence (decreased precision). Coarse screening (greater than 60 mesh) of the dried or wet sample results in a decrease of about one-third of the sulfur fluorescence even with dried samples. Table 7 summarizes the results of the experiments with samples of different % water content.

**Table 7: Effect of Water Content on S (cps) and Regression**

	<b>Site #3 1.8 % S</b>		<b>Site #6 0.4% S</b>	
	R <sup>2</sup>	S (cps)	R <sup>2</sup>	S (cps)
<b>Method 1</b>	0.992	221.4	0.982	48.2
<b>Method 2</b>	0.989	175.0	0.898	29.5
<b>Method 3</b>	0.818	152.2	0.786	30.3

The effect of dilution by water for other elements showed the same qualitative linear decrease in fluorescence with increase in water content; however the slope of the regression varies with the element. Helium increased the S/N by 30% for sulfur, leading to greater sensitivity.

For the most accurate and precise work, it is essential that samples are dried, ground, and sieved (as recommended) to achieve a fine degree of homogeneity. In addition, if the highest accuracy is required for sulfur determination, a calibration curve must be constructed with a number of different standards with sulfur content approximately that of the unknown.

The Niton XRF XLt 500He can be used for semiquantitative sulfur analysis (+/- 20%) portably in the field with wet sediment samples. It is recommended that one remove as much water from the samples as possible in the field before taking measurements, and then correct for the water content in the samples, which can be determined at a later time. A handheld XRF device has been shown to be a versatile and easy to use analytical method for a number of metals and non-metals. Use of the helium purge extends the utility of the device by permitting the analysis, not only of the heavy metals, but elements that could not previously be analyzed in the field with a hand-held unit. The precision of the unit is excellent and the limit of detection can be quite low with proper sample preparation.

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